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DESCRIPTION

Process for producing a corrosion- and wear-resistant layer on a substrate and a material for same

The invention concerns a process for producing a corrosion- and wear-resistant layer on a substrate by spraying on an iron oxide-based material. The invention further concerns a material for producing a corrosion- and wear-resistant layer on a substrate which is applied by thermal spraying with that process.

DE 30 48 691 A1 discloses a process of that kind, with which a piercer bar for a piercing and drawing mill is coated; a protective layer is formed on the bar surface by spraying on in a molten state a powder which extensively consists of iron oxide; the aim is that such a piercing bar can be inexpensively produced and is to be of excellent durability and is to afford better insulating and sliding properties. For that purpose, the iron oxides involved are the compounds FeO, Fe_3O_4 and Fe_2O_3 or mixtures thereof, which make up more than 50% by weight of the powder. It is also possible to use oxides of chromium, nickel, copper and manganese or metals from the group consisting of iron, chromium, nickel, cobalt, copper and manganese.

DE 34 35 748 A1 describes the use of a laser anemometer whose measurement volume is displaceable relative to a hot gas jet, for ascertaining the particle speeds in thermal spraying. The particle flow density is ascertained by a particle counter which counts the number of spray particles respectively flying through the measurement volume. The mean particle trajectories and the fusion state are calculated in a digital data processing apparatus.

Anti-corrosion and anti-wear layers are usually applied from powder mixtures of various kinds to surfaces to be protected in manufacture or for maintenance purposes. Thermal spraying processes or vapor deposition processes such as CVD (chemical vapor deposition) or PVD (plasma vapor deposition) are mainly used for that purpose. The CVD and PVD processes make it possible to apply thin anti-corrosion and anti-wear layers based on an oxide or hard substance, in particular in mass production. Electrochemical or galvanic processes are also used.

Layers of a layer thickness of more than 0.1 mm are primarily provided by means of thermal spraying. The corrosion- and wear-resistant layers produced by thermal spraying mostly involve metallic or oxidic layers in which hard substances are incorporated for enhancement purposes.

One of the major problems with regard to thermal spraying processes is the production of layers of constant properties and quality. For that reason, it was possible for thermal spraying processes to be used only to a limited extent on substrates or parts with high demands in respect of quality in mass production.

Tests with a choice of the material in regard to its chemical composition or its form - for example on the one hand the wire diameter of a filling wire or on the other hand the grain size distribution and the grain shape of the spray powder - did not result in an adequate increase in quality. Changes to the spray installations also did not contribute to better quality.

Attempts were made to provide protection from wear and corrosion by means of layers applied by thermal spraying, comprising iron oxide or magnetite. In all attempts of that kind it was found that the quality of the respective layer, in regard to the layer structure, could be safeguarded to some degree only at great cost.

In consideration of those factors, the inventor set himself the object of improving the production of a constant, wear- and corrosion-resistant surface coating on an oxide base, by means of thermal spraying.

That object is attained by the teachings of the independent claims; the appendant claims set forth advantageous developments. The scope of the invention also includes all combinations of at least two of the features disclosed in the description, the drawing and/or the claims.

In accordance with the invention the iron oxide-based material which has at least 20% by weight - preferably more than 30% by weight - of magnetite (Fe_3O_4 and/or $FeFe_2O_4$) is applied by on-line controlled flame spraying, in particular high-speed flame spraying, or plasma spraying, in particular plasma spraying in air or vacuum, high-power plasma spraying (HPPS), shroud plasma spraying (SPS) or by on-line controlled wire flame spraying or arc wire spraying, and in that procedure the layer comprising the material is monitored by an on-line monitoring and control system.

In accordance with the invention, for applying the wear-resistant and/or corrosion-resistant layer, all thermal spray processes such as autogenous flame spraying, high velocity flame spraying (HVOF spraying), plasma spraying in air (APS), shroud plasma spraying (SPS), vacuum spraying (LPPS), high-power plasma spraying (HPPS), autogenous wire spraying or arc wire spraying can be used.

On-line monitoring and control is effected with a combination of various processes which make it possible to measure the temperature of the particle or the degree of melting, the particle size, the speed, the impingement thereof on the substrate and the rise in temperature of the layer and the substrate during the spraying operation. The measurement signals are then passed to the computer of a control installation for the spraying apparatus and the flame parameters and the power involved are matched to the values in question.

The inventor therefore found that it is possible to provide a coating which satisfies the above-mentioned requirements if the material used is

an iron-based oxide to which metals, hard substances or intermetallic compounds are added, depending on the corrosion or wear problem to be resolved. The material must be produced in accordance with a given production process; in accordance with the invention a powder grain produced from the material mixture in powder form by spray drying, with good flow properties, is proposed, and a powder grain which is resistant to separation of the mixture and which is produced from the material mixture in powder form by means of an agglomeration process.

The spraying installation is equipped with an on-line monitoring or control system for supervision purposes in order to be able to produce layers with a high level of quality and uniform properties by a spraying-on procedure.

What has been found desirable for that purpose is on-line monitoring and control by means of an ITG-camera directed on to the spray jet, an LDA-detector with an LDA-laser and an HSP-head, or on-line monitoring by means of an ITG-camera directed on to the spray jet and an HSP-head of a measurement body.

Desirably, the particle speed in the spray flame is to be measured by the on-line monitoring and control, for example by a laser Doppler anemometer, on the basis of a beam which is emitted from a laser device and which is broken down into two partial beams by an optical transmission system.

In accordance with another feature of the invention the particle temperature in the spray flame is observed by the on-line monitoring and control system, by means of a high-velocity pyrometer. That is effected for example by means of infra-red thermography.

It has also been found to be desirable to measure the amount of gas, for example an amount of plasma gas, by the on-line monitoring and control system.

By virtue of the on-line monitoring and control system it is also possible to evaluate a measured current-voltage characteristic or to measure an amount of powder which is fed to the spray flame.

In accordance with the invention the layer material for production of the corrosion- and wear-resistant layer has at least 20% by weight and preferably more than 30% by weight of magnetite (Fe_3O_4, also with additions of Fe_2O_3); this may involve pure magnetite (Fe_3O_4) or a material comprising magnetite and at least one further metallic material, possibly also magnetite and at least one intermetallic compound.

In addition a material with an addition of carbide or carbides or nitride or nitrides or silicide or silicides or boride or borides or oxide or oxides has proven to be advantageous or a material whose additives are mixtures of metals, intermetallic compounds, carbides, nitrides, silicides, borides and/or oxides.

The additions of up to 50% by weight and preferably up to 40% by weight to the magnetite may be for example Cr, CrNi or ferritic steels.

In regard to the hard substances, carbides, nitrides, silicides, borides and oxides have proven successful as additions. In regard to the carbides, carbide-forming agents such as tungsten, chromium, molybdenum, niobium, tantalum, titanium, vanadium or the like are suitable. The addition of the carbides should be limited to at most 30% by weight, preferably 20% by weight. With the borides and nitrides as additives at that level, improvements in the properties were found. Oxidic additions of chromic oxide (Cr_2O_3) of an order of magnitude of between 1 and 40% by weight, preferably between 5 and 30% by weight, also show good results.

In order to achieve a high quality the spray materials in powder form must involve a grain size of between 0.05 and 150 μm, preferably between 0.1 and 120 μm. In regard to the mixtures of various powder materials, it is recommended that they should be agglomerated or spray-

dried in order to prevent the mixture from separating and in order to improve the flow characteristics.

When using spray materials in wire form, with a high proportion of magnetite, it is possible in accordance with the invention to produce a filling wire from a metal sheath and magnetite powder.

In accordance with the invention, for applying the wear-resistant and/or corrosion-resistant layer, all thermal spray processes such as autogenous flame spraying, high velocity flame spraying (HVOF spraying), plasma spraying in air (APS), shroud plasma spraying (SPS), vacuum spraying (LPPS), high-power plasma spraying (HPPS), autogenous wire spraying or arc wire spraying can be used.

On-line monitoring and control is effected with a combination of various processes which make it possible to measure the temperature of the particle or the degree of melting, the particle size, the speed, the impingement thereof on the substrate and the rise in temperature of the layer and the substrate during the spraying operation. The measurement signals are then passed to the computer of a control installation for the spraying apparatus and the flame parameters and the power involved are matched to the values in question.

The inventor therefore found that it is possible to provide a coating which satisfies the above-mentioned requirements if the material used is

an iron-based oxide to which metals, hard substances or intermetallic compounds are added, depending on the corrosion or wear problem to be resolved. The material must be produced in accordance with a given production process; in accordance with the invention a powder grain produced from the material mixture in powder form by spray drying, with good flow properties, is proposed, and a powder grain which is resistant to separation of the mixture and which is produced from the material mixture in powder form by means of an agglomeration process.

The spraying installation is equipped with an on-line monitoring or control system for supervision purposes in order to be able to produce layers with a high level of quality and uniform properties by a spraying-on procedure.

What has been found desirable for that purpose is on-line monitoring and control by means of an ITG-camera directed on to the spray jet, an LDA-detector with an LDA-laser and an HSP-head, or on-line monitoring by means of an ITG-camera directed on to the spray jet and an HSP-head of a measurement body.

Desirably, the particle speed in the spray flame is to be measured by the on-line monitoring and control, for example by a laser Doppler anemometer, on the basis of a beam which is emitted from a laser device and which is broken down into two partial beams by an optical transmission system.

In accordance with another feature of the invention the particle temperature in the spray flame is observed by the on-line monitoring and control system, by means of a high-velocity pyrometer. That is effected for example by means of infra-red thermography.

It has also been found to be desirable to measure the amount of gas, for example an amount of plasma gas, by the on-line monitoring and control system.

By virtue of the on-line monitoring and control system it is also possible to evaluate a measured current-voltage characteristic or to measure an amount of powder which is fed to the spray flame.

Further advantages, features and details of the invention will be apparent from the description hereinafter of preferred embodiments and with reference to the diagrammatic drawings in which:

Figure 1 shows an on-line control and monitoring system for a plasma installation,

Figure 2 shows an installation for infra-red thermography (ITG) and for high speed pyrometry (HSP) in the thermal spraying procedure,

Figure 3 is a diagrammatic view relating to infra-red thermography (ITG),

Figures 4 and 5 each show an installation for high speed pyrometry (HSP),

Figure 6 shows an embodiment of a laser Doppler anemometer (LDA),

Figure 7 is a diagrammatic view relating to particle shape measurement in flight (PSI = Particle Shape Imaging),

Figure 8 shows particle temperature measurement in flight (PTM = Particle Temperature Measurement), and

Figure 9 is a diagrammatic view relating to the measurement of particle temperature and speed.

For the purposes of applying wear and/or corrosion layers, it is possible to use all thermal spraying processes such as autogeneous flame spraying, high velocity flame spraying (HVOF), plasma spraying in air (APS), so-called shroud plasma spraying (SPS), plasma spraying in vacuum (LPPS), high-power plasma spraying (HPPS), autogenous or arc wire spraying. On-line monitoring and control is effected by a combination of various processes which make it possible to measure the temperature of the particle or the degree of melting, the particle size, the speed, the impact thereof against the substrate and the rise in temperature of the

layer and the substrate during the spraying operation. The measurement signals are then fed to the computer of the control portion of the thermal spraying installation in order to be able to adapt the flame parameters and the power to the measured values.

An on-line control and monitoring system as shown in Figure 1 for the flame or the spray jet 10 of a spray gun, indicated at 12, or the like spray device 12, with a powder feed 16 arranged in front of the torch nozzle 14 thereof, has above the spray jet 10 an ITG-camera 18 - that is to say an infrared thermography camera - and a laser Doppler anemometer (LDA-detector) 20 for an LDA-laser 22 which can be seen beneath the spray jet 10; beside same is disposed an HSP-head 24 - HSP = high speed pyrometry - , which is connected to a coil-like measurement body 26.

As shown in Figure 3, for the purposes of measuring the substrate temperature T_s and the coating temperature T_c by means of infra-red thermography, a substrate 30 which is to be provided with a coating 32 is disposed in the recording region of an ITG-camera 18. Extending from the camera 18 is a glass fiber cable 36 which goes to a video PC card indicated at 42 - 500 KHz - . Connected thereto is a computer 46 with a monitor 48, with which here a temperature pick-up device 50 is associated.

Referring to Figure 4 the HSP-head 24 is directed to the coating 32 of the substrate 30 for measuring the cooling rate or the coating temperature Tc by means of high speed pyrometry (HSP). The HSP-head 24 is connected by way of an AD-converter 52 to a computer 46 which has a storage element 44 and a monitor 48. A high speed pyrometer with HSP-head 24, AD-converter 52 and a computer 46 which includes a user menu 54, a control menu 56 and graphic software 58 can be seen in Figure 5.

Optimisation of the spray parameters can be achieved with the process of so-called laser Doppler anemometry (LDA), which involves a low level of expenditure in terms of time and cost. In the preferred dual-

beam procedure the beam 60 of an argon-ion laser indicated at 62 (λ = 514.5 nm, P = 150 mW) is divided by an optical transmission system 64 into two partial beams 60_a, 60_b of equal intensity. The two partial beams 60_a, 60_b are focussed into a stationary measurement volume 66. There they intersect at a defined angle in such a way as to afford an interference pattern which is intensity-modulated in strip form. A particle of the spray jet 10 which flies through that strip pattern produces a stray light signal 68 which is variable periodically in respect of time for an optical receiving system with photodetector 70. The modulation frequency of the stray light signal 68 is proportional to the speed component of the particle perpendicularly to the interference strip system. The frequency of the LDA-stray light signals is a measurement in respect of the local density of the particles in the plasma spray jet 10. Location-resolved measurement of relevant particle parameters is possible by scanning the jet. It is possible to obtain therefrom results such as speed distribution, trajectories and residence times of the particles.

As it is not possible to implement individual determination of shape and size of a spray particle by LDA, then in accordance with Figure 7 particle shape imaging (PSI) is used, an imaging process for location-resolved determination of size and shape of individual powder particles in plasma spray jets 10. The measurement principle is based on telemicroscopic imaging of the shadows of the particles, the measurement method has the advantages of a high level of light strength in comparison with stray light processes and at the same time a reduction to the desired image information. Similarly as in the case of laser Doppler anemometry, the beam 60 of an Nd-YAG continuous-wave laser 60_a (λ = 532 nm, P = 100 mW) is divided up at a beam divider 72 with mirrors 74 into two partial beams 60_a, 60_b of equal intensity, which are crossed by means of the mirrors 74 in the object plane E of the television microscopy objective lens of a television microscope 76. The use thereof makes it possible to maintain a safety distance of 600 mm in relation to the object being

measured. With an imaging scale of 1:10 a degree of optical resolution of 2.7 μm is still achieved. The imaging system comprises a CCD-camera 78 with an upstream-connected micro-channel plate (MCP) image amplifier of a minimum exposure time of 5 ns.

The geometrical dimensions of the 512 x 512 pixel CCD-chip and the depth of focus range of the objective lens give a measurement volume of 410 x 410 x 940 μm^3.

For the situation where a particle in the measurement volume is disposed precisely at the object plane E, partial shadows are generated by both beams 64, 64_a, which partial shadows are completely coincident upon imaging on to the CCD-chip and thus form a full shadow. In proportion to the spacing of the particles from the object plane E, the partial shadows in the image plane move away from each other and the full shadow region decreases. The position of a particle relative to the object plane E can be determined with that effect. The area and contour of the shadow image give information about the size and shape of the particle. The LDA-interference strip pattern which is also imaged supplies the size scale in that respect. With the minimum exposure time of the MCP-CCD-camera of 5 ns, that gives a value of 500 m/s as the maximum particle speed, at which the movement blur does not exceed the optical resolution capability.

In the process of so-called in-flight particle diagnosis - in which respect attention is directed to Figure 8 - then irrespective of the spray process up to 200 individual particles can be measured per second at each point in a spray jet simultaneously in respect of their surface temperature, speed and size. A displacement unit (not shown) additionally permits rastering of a plane perpendicularly to the spray jet 10 so that it is possible accurately to determine the distribution of the particles in the spray jet 10. The operation of determining temperature is effected by means of dual-wavelength pyrometry at $995 \pm 25\ \mu m$ and $787 \pm 25\ \mu m$. In that case the particles are treated as gray bodies so that there is no need for the exact degree of emission to be known for temperature

measurement. The system includes imaging of a dual-slit mask 80 measuring 25 μm x 50 μm - at a measurement head 82 - at a focal point at about 90 mm spacing with a high depth of focus. That affords a measurement volume which, corresponding to the graphic view above Figure 10, is characterised by two visible and an interposed shadow region. The measurement volume is about 170 x 250 x 2000 μm^3. The characteristic radiation of individual particles which fly through that measurement volume is recorded by way of two IR-detectors at two different wavelengths. Two temperature peaks consequently occur through the two partial measurement volumes. The spacing in respect of time of the two peaks is a measurement in respect of the speed of the particle. The principle corresponds to that of a light barrier arrangement.

This procedure makes it possible to determine particle surface temperatures of between 1350°C and 4000°C. The measurable particle size essentially depends on the temperature of the particles. It is limited downwardly to about 10 μm and upwardly to about 300 μm and is determined by the absolute energy which is irradiated from the particle and which is proportional to the square of the diameter. The measurable speed range is 30 m/s - 1500 m/s.

The view in Figure 9 links to that shown in Figure 1 and shows measurement of particle temperature and speed by means of an HSP-head 24.

The procedure involved will be described in greater detail by way of some examples of use:

EXAMPLE 1

A casing mold for aluminum casting is to be provided with a layer which prevents material from baking on and sticking in the mold.

For the tests, a coating, between 0.2 and 0.5 mm in thickness, of a material composition of:

95.5% by weight	magnetite (Fe_3O_4)
4.5% by weight	iron oxide (Fe_2O_3)

was selected; in the case of aluminum and alloys thereof that is intended to prevent the material from sticking and baking on. Further properties of the spray powder were:

grain size > 5 μm

< 45 μm

with a grain size of the initial material > 1.5 μm.

The grain structure of the round grains is produced by agglomeration by means of spray drying.

The application operation was effected by plasma spraying in air (APS) with a power of 60 KW and argon/hydrogen plasma, which was provided with an on-line control unit as shown in Figure 1; the particle speed and particle temperature are there measured in-flight in order to control the plasma spray jet in such a way that the necessary degree of melting-on of the particle is achieved.

The mold surface to be coated was positively cooled with CO_2, with the aim of minimising oxidation upon particle impact.

The layer produced in that way by thermal spraying was then ground and tested in an aluminum foundry. In that case it was found that the material was prevented from sticking and baking on the mold and the expensive procedure of spraying the mold with a mold release agent can be avoided.

EXAMPLE 2

A protective layer, between about 1.0 and 2.0 mm in thickness, is to be applied to the transport roller of a paper making machine, to provide protection from wear and corrosion in aqueous solutions. By virtue of operation occurring in aqueous solution that protective layer must be of a high density (at least 99% of the theoretical density). The spray material used was a filling wire of the following composition:

Filling:	magnetite (Fe_3O_4)
Sheath:	Ni/Cr 80/20 with about
	30% by weight of the filling wire

The grain size of the starting material for the filling was > 1.0 μm.

For spraying on the protective layer, use was made of an arc spraying installation equipped with an on-line control and monitoring system, for processing filling wire, the control system used being a combination of the two systems shown in Figures 1 and 3. Positive cooling was effected with CO_2 and air.

After the coating operation the roller which was 200 cm in length was ground to a surface quality of Ra 0.4 μm. No flaws could be found in the layer when the surface was checked with a binocular magnifying device with a magnification of x = 20.

After a test run of six months, the transport roller fitted in the paper making machine, together with a chromium-plated roller, was removed, and the surfaces were examined. That examination revealed that no flaws or attacks due to corrosion or wear could be found on the transport roller coated by plasma spraying for the test. The chromium-plated comparative roller exhibited the attack which is known for that operating time.

EXAMPLE 3

In regard to the piston rings of internal combustion engines, improvements are continuously being demanded in the coatings in development thereof. After a number of considerations tests were now to be carried out with a pure magnetite coating. The problem of such a coating comprising pure magnetite (Fe_3O_4) lies in the unwanted possibility that the magnetite could be oxidised to form Fe_2O_3 in the spraying operation, which would result in a loss of the desired good properties.

Pure magnetite was used as the spray material. The grain size of the spray powder was as follows:

< 37 μm

> 5 μm,

while the grain size of the starting material was:

< 0.5 μm.

The spray powder of round grain shape was produced by agglomeration in spray drying.

To apply the coating, use was made of a plasma installation equipped with a gas shroud and an on-line control unit, for plasma spraying in air (APS), of a power of 80 KW. The parameters which were to be kept constant, for controlling the plasma installation, were as follows:

- particle speed;
- particle temperature;
- substrate temperature;
- fusing of the particle.

CO_2 was used to afford positive cooling for the substrate and the layer during the spray operation. The shroud used to afford protection from oxidation was operated with very pure argon.

The piston rings coated with pure magnetite using that process exhibited a high level of quality upon being checked and afforded good results in a continuous running test in engines.

EXAMPLE 4

A dip device for a salt bath operating at 500°C for the heat treatment of relatively small parts has a high level of corrosion after an operating time of approximately one week.

The attempt was now to be made to prevent the wear and corrosion by virtue of the application of a magnetite/carbide protective layer. The material used was a mixture comprising:

75% by weight of magnetite,

25% by weight of chromium carbide.

The thermal spraying process for applying the layer in a thickness of 80 μm was a high velocity flame spraying procedure (HVOF) in which control was effected in an on-line mode. After the spraying operation the layer was polished.

Under the same conditions, the service life of the layer applied in that way was two weeks.

EXAMPLE 5

A hydraulic cylinder for underground mining of a length of 1000 mm and a diameter of 200 mm was to be provided with a protective layer to afford protection from corrosion and wear. Hitherto, a galvanically applied hard chromium layer had been used as the protective layer, but it had a service life of at most two months due to the occurrence of hairline cracks in the layer.

A protective layer of the following composition was now selected:

70% by weight of Fe_3O_4 (magnetite),

30% by weight of Cr_2O_3 (chromium oxide)

wherein the grain size of the agglomerated spray material was:

$> 5\ \mu m$

$< 37\ \mu m$.

An HPPS (high power plasma) installation with a power of 200 KW was used to apply the protective layer in a layer thickness of between 1.0 and 1.5 mm, the installation being provided with an on-line control system to maintain the precise spray parameters and avoid oxidation.

The protective layer produced in that way was checked after a period of two months and it was found that the surface of the layer exhibited no attacks by corrosion or wear. The operating life of the layer was nine months.

EXAMPLE 6

The piston of a vacuum pump of a diameter of 20 mm and a length of 500 mm was to be provided with an anti-wear and anti-corrosion layer. The material used was an agglomerated spray powder of the following composition:

80% by weight Fe_3O_4

20% by weight Ni_3Al

and of a grain size:

$> 5\ \mu m$

$< 45\ \mu m$.

An LPPS-installation with a power of 40 KW, provided with an on-line control system, was used for the coating operation.

In subsequent use the coating produced in that way exhibited very good results in comparison with conventional normal pistons.